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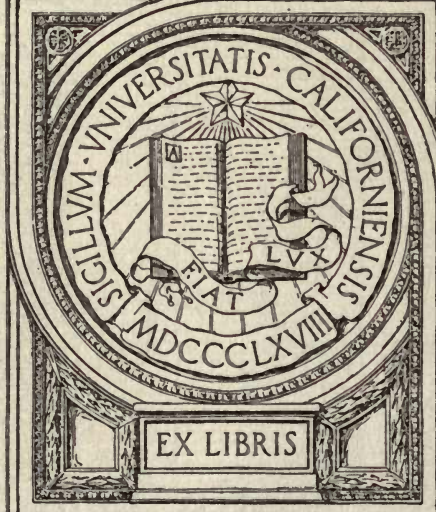
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A Spectrographic Study by Means of a Grating (Replica) Spectroscope and The Determination of The Wave Lengths of The Arc Spectrum of Tantalum

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AS A THESIS, FOR THE DEGREE OF DOCTOR OF SCIENCE,

BY ALLAN F. ODELL, M. S.

UNIV. OF
CALIFORNIA

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ACKNOWLEDGMENT.

I wish to express my sincere appreciation and thanks to Dr. William L. Dudley, of this University, at whose suggestion this research was commenced, and by whom it has been directed.

469862

As a token of esteem and affection to my
old class-mate

ERNEST WILLIAM GOODPASTURE

INTRODUCTION.

The original object of this research was to investigate the contents of rare elements in some of the clays of the South; and for this purpose, samples were collected from as many different points as possible.

The manner in which the investigation was to be carried out, was to separate the clay into its various constituents, and examine these in the spectroscope, and, if unusual elements were found, to estimate the quantity. To give an example, a clay was treated thus: It was first qualitatively analyzed for the ordinary elements, as iron, aluminum, manganese, calcium, magnesium, potassium, sodium, etc. The precipitates obtained for these metals were dried, powdered, and put in the arc for photographing the spectrum. The resulting spectographs were examined, and the lines carefully measured. In this manner, the spectra of the rare elements would identify their presence without making the tedious qualitative examination for them in the first instance necessary.

RESIDUES CONTAINING DOUBTFUL ELEMENTS.

In the first set of clays examined, three specimens from Spruce Pine, Alabama, a residue was obtained which gave lines of Ti, and another element, which we could not identify from its spectrum. The method by which this residue was obtained is as follows: The clay is finely pulverized and heated with a mixture of eight parts conc. sulphuric and two part conc. nitric acid, until solution has taken place and only a white siliceous residue is left. By this method the majority of the elements are taken into the solution. It is diluted with water and the siliceous matter filtered off. The Fe and Mn and some rare elements are precipitated from the filtrate by adding an excess of KOH. The solution is again filtered and the precipitate washed on the filter. The precipitate is then dissolved in HCl, and the resulting solution treated with NH_4OH, until precipitation occurs, (NH_4) 2Sx is added until the hydroxide which was first precipitated, is changed into sulphide. H_2SO_3 is then added until the solution clears, leaving a white precipitate. Ti, Cb, Ta, etc., remain in the precipitate, which is filtered off and washed. The Fe, Mn, Cr, etc., will be in the filtrate. The precipitate is dried, and removed from the paper, and fused with Na_2CO_3 in a platinum crucible. The fusion is digested in cold water and filtered. The precipitate is treated with HCl, and to the resulting solution $Na_2S_2O_3$ added. A precipitate is gotten which is designated as precipitate A. This precipitate was examined under the spectroscope, and will be referred to later. If the filtrate from precipitate A is treated with KOH, another precipitate is gotten, which is precipitate B, and which has not yet been investigated, as the quantity obtained was too small. The filtrate from the Na_2CO_3 fusion is made acid with HCl, and the CO_2 expelled by boiling, NH_4OH is then added, and the excess expelled by boiling. Another precipitate is obtained. This, also, has not been examined.

Precipitate A gave lines for Ti, and was contaminated by traces of Fe; but there were also other strong lines present, which could not be identified in the spectra of either of these elements.

As tantalum occurs widely distributed, and associated with titanium, some lines of the former were suspected of being pres-

ent in the spectrum of precipitate A. And as no arc spectrum of tantalum has been made heretofore, and as the continued recurrence of this element would present serious difficulty in the future work on clays, the arc spectrum of tantalum has been made between λ3200 to λ6300.

The apparatus available would only permit of the measurement of the lines to the fourth place, which is sufficiently accurate for all practical work.

THE ARC USED.

The first arc used was a closed lantern with carbon poles, but as so many bands occurred in the carbon spectrum, they obscured the fainter lines, and the carbon poles with the closed lantern were discarded and replaced by a hand feed lantern using copper poles. As copper gives a sharp spectrum with lines widely distributed, it served perfectly. The impurity in it is chiefly Fe, and this assists in finding standards for measurement. The poles are 5-16 of an inch in diameter, and are turned down a half inch from the end to about 3-16 of an inch. The lower pole is cupped out for receiving the substance. The current used was about 104 volts and four to six amperes. The bottom pole containing the substance, was used as the positive pole. (Fig. I.)

An attempt was made to secure spark spectra of some of the clay residues, but as these were usually in the form of a fine powder, the spark, on turning on the current, would brush the substance off the pole immediately.

In taking the spectra from the arc, it was found that by shifting the upper pole slightly, the arc could be kept constantly on the fused substance on the lower pole, thereby diminishing the copper cpectrum and intensifying the spectrum with the substance to be examined.

Figure 1

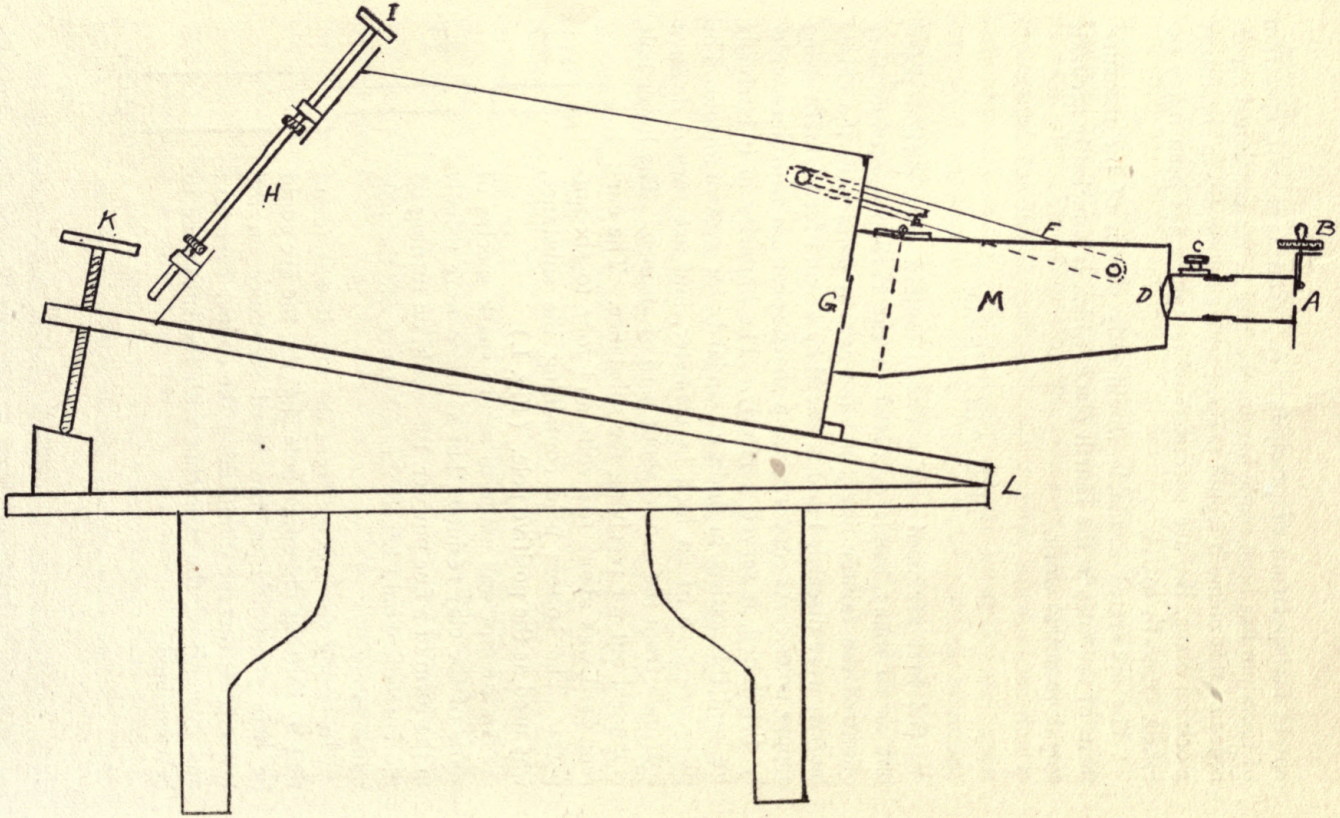


Figure 2

THE SPECTROGRAPH.

The spectograph used is one of special construction, and designed by Dr. Dudley, and made so that the entire spectrum between λ3000 and λ6500 can be taken on one plate.

Its construction will be easily understood from the diagram. (Fig. 2.) A is the slit, regulated by the micrometer screw B which adjusts the slit in fortieths of a millimeter. C is the screw adjustment which focuses the light from A on to the lens D, which parallels the rays upon the grating G. From thence they are dispersed upon a vertical slit at H, behind which is arranged the photographic plate. K is the screw which raises and lowers the table L. E is a hinge, regulated by F, which raises and lowers the portion of the spectrograph at M so that the extreme red or violet may be taken by raising or lowering it, respectively. I is an arrangement for moving the photographic plate before the slit H. Upon this plate about twelve spectra can be taken. This spectrograph has a focus of 2 1-2 feet, and uses a replica grating with 20150 lines to the inch. The size of the plate used is 3¼ by 4 inches. The instrument is capable of transmitting wave lengths to about 2600.

PURIFICATION OF TANTALUM.

The tantalum, in the form of Ta_2O_5, was prepared from tantalite obtained from Pilbarra Dist. W., Australia. The method used in the separation and purification of the tantalum is a modification of the original method of Wolcott Gibbs for the preparation of Columbium from Columbite,* and is as follows: The finely powdered tantalite is fused with twice its weight of KHF_2 in a platinum dish, until the tantalite is dissolved, and the excess of HF is driven off. The fusion is dissolved in water, and the gangue filtered off. The filtrate from this is evaporated a little and allowed to stand to crystallize. If crystals do not form on cooling, it is evaporated more and stood aside again. In this manner successive small crops of tantalum potassium fluoride crystals are prepared. These are kept separate, and a specimen of Ta_2O_5 is prepared from the first crop, by the method explained later, and is examined in the spectroscope. This first crop of crystals of the double fluoride is again dissolved in water. And fractionated further, a specimen of Ta_2O_5 is also prepared from

*Am. J. Sc. & Arts 37, 357.

the next first crop and examined under the spectroscope similarly. This fractionation and recrystallization of the double fluoride is continued until the spectrum of the specimen of Ta_2O_5 from the last crops shows no loss of lines, indicating that the impurities have vanished through repeated recrystallization. This final crop of double fluoride crystals is dissolved in water and treated with H_2S as a precaution to insure the absence of Sn, W, etc. The precipitate, if any, is filtered off, and the filtrate treated with concentrate H_2SO_4, and evaporated to dryness. The residue is treated with water and Rochelle salt. All metals will go into solution except the tantalum, which is left as Ta_2O_5, and which, on washing well, will be found in a sufficiently pure condition for spectroscopic work.

THE METHODS OF MEASUREMENT.

The measurement of the lines is made in two different manners. First the measurement with the comparator, by which means a relative number is given to each line. A curve is then plotted upon cross section paper from which this number can be converted into wave lengths. The error of this method is about 0.5 Angström unit.

The second manner is by means of the projection method. The plate upon which is the spectrum to be measured is put in an ordinary projection lantern and the image thrown upon a screen from twelve to sixteen feet removed. The lines are measured by means of a centimeter scale, which will be more fully explained later.

THE COMPARATOR.

The comparator mentioned above was made to order by Zeiss & Co. It consists of two moderately high power stationary microscopes mounted six inches apart. Beneath these is a movable stage, half of which has a scale graduated in tenths of millimeters on its surface, which slides back and forth under, and is read through the right-hand microscope. The other half of the stage is constructed so that it will hold a plate. It has in its middle a slit three-eighths of an inch wide, which traverses the entire length of the surface that is intended to hold the plate. When the stage slides back and forth, this slit is beneath the left-hand microscope, and is free to receive the light reflected from

a mirror placed beneath the stage, directly under the microscope.

The microscopes are about twenty diameters in power, and have the usual focusing adjustment. Each has beneath the eye-piece a stationary pointer, and two parallel wires moving horizontally and governed by a micrometer screw on the outside. The pointer of the left-hand microscope is placed directly over the lines to be measured, and the width of the line may be determind by the parallel wires and micrometer screw attached to this microscope. The pointer of the right-hand microscope has the parallel wires placed directly across it, at which point the micrometer screw reads zero. The parallel wires are then moved across the nearest scale number, and, then reading of the fractions taken on the micrometer. In this manner, measurement are made to the one-thousandth of a millimeter. The spectrum to be measured is put upon the slit under the left-hand microscope. The stage is then adjusted so that some arbitrary number is under the right-hand microscope, for example, 40.000. The plate is then adjusted under the microscope so that some known line, which is used as a standard, comes between the parallel wires. The stage can be drawn back now so that the far edge of the spectrum is under the microscope, and as each line comes between the cross wires, the scale is read at the right-hand microscope. For example, we find lines in the copper spectrum on numbers 39.025, 41.000, 51.060, etc., when the line λ5179 is set on 40.000.

THE COMPARATOR METHOD.

Now to convert these numbers into wave lengths, a chart must be drawn upon cross section paper. Copper has in its spectrum several prominent lines which are easily recognized. There are three lines in the red, λ5218, λ5153, and λ5105, which read on the comparator 39.025, 40.645, and 41.800 respectively; two lines in the green, λ4651 and λ4275, which read on the comparator 52.900 and 62.340; two lines in the violet, λ4062 and λ4022, on the comparator 67.720 and 68.710. There occur also, several iron lines with the copper in the spectrum, as the copper was not pure; and these assist in plotting the curve.

A piece of cross section paper is taken which has along one coordinate, the wave length numbers, and along the other the com-

parator scale numbers. (Fig. 3.) As the measurement of the plate commenced in the red, the comparator numbers read up, while the wave lengths read down. A place is now found on the chart along the wave length co-ordinate for λ5218, and along the comparator scale co-ordinate 39.025. If the two points found are extended, along the perpendicular and horizontal lines of the cross section paper, they intersect in a point, which is the starting point of the curve. The other lines, of which we know the wave lengths and the comparator reading, are placed in a similar manner. When all the points have been found, they are connected by a line which forms the curve. In this case, where the diffraction grating was used, the curve is so slight as to approximate a straight line. Now the method by which the wave lengths are gotten, is to take the comparator reading, find its place along the proper co-ordinate, extend it out until it strikes the curve, and drop a perpendicular from this point to the wave length co-ordinate, and the wave length is read off this.

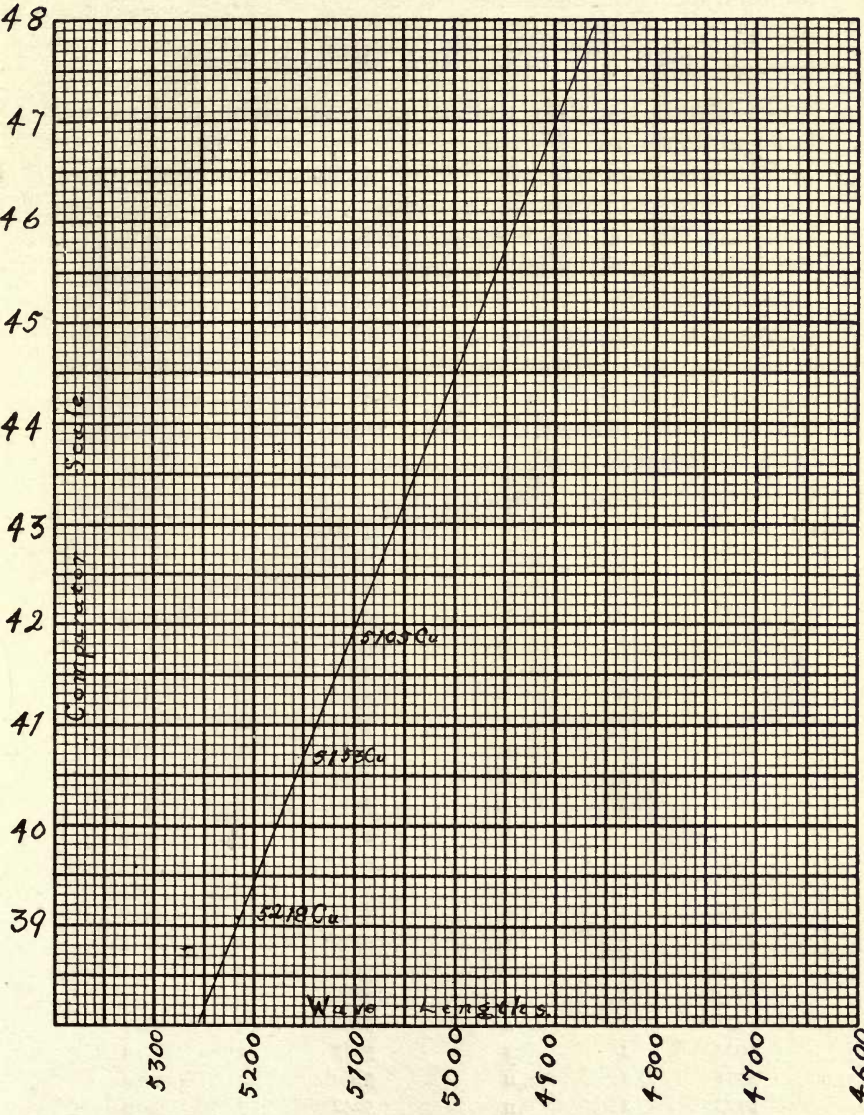
THE PROJECTION METHOD.

The projection method has the double advantage of being much simpler and more accurate, and the relative intensities of the lines may be determined with greater facility, but at the same time, the faint lines cannot be seen and measured so easily.

For this purpose it is only necessary to place the plate in the lantern, and project the image on a screen twelve to sixteen feet away. The lantern is shifted back and forth until the distance between λ5218 and λ5105 is, we will say, thirty centimeters. The wave length difference between these two lines, as can be seen, is one hundred thirteen Angström units, the linear difference is thirty centimeters, hence thirty cm. equals 113 A. U., one m. m. equals 113-300 A. U. Now to measure any line between the two standards, one must get the linear distance from either of the standards to this line, and convert the distance into A. U. as shown above, and add it to or subtract it from the standard, according to whether the measurement is made in the direction of the red or violet end.

The dispersion not being precisely equal for all colors, new values of A. U. in m. m. must be taken between new standards, as the measurement progresses along the spectrum.

Seed's Panchromatic plates were used at first, and then Cramer's "Pan Iso Plates" were adopted, the latter being very sensitive to the red rays.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47
46
45
44
43
42
41
40
39
Comparison Scale
5163 Cu
5153 Cu
5218 Cu
Wave Lengths
5300
5200
5100
5000
4900
4800
4700
4600

Figure 3

About twelve dozen plates were developed with from eight from twelve spectra on each plate, making a total of about eleven hundred spectra examined.

THE ARC SPECTRUM OF TANTALUM.

Following, the wave lengths of the tantalum spectrum will be given from $\lambda 3200$ to $\lambda 6300$.

The intensities range from 1, for the lines easily visible, to 10, for the strongest lines, in the copper spectrum. 0 is used for lines just visible. An n denotes nebulous, a line not sharply defined; s denotes sharp; b denotes band; and is inclosed in brackets, the wave lengths of the two edges being given. A D following a character letter (as sD) means double. After some of the lines will be seen the symbol of an element followed by a question mark, indicating that the probability is that the line belongs to the element mentioned, which might have occurred in the spectrum as an accidental impurity.

Wave Length.	Intensity.	Character.	Wave Length.	Intensity.	Character.
6268	2	n	5870	3	s
6264	2	n	5863	1	s
6252	2	n	5859	1	s
6248	2	n	5856	1	s
6203	1	n	5848	1	s
6195	1	n	5847	1	s
6049	1	s	5842	2	s
6041	1	s	5837	2	s
6034	4	s	5830	1	n
6010	1	sD	5820	1	n
6000	1	s	5816	0	s
5996	1	s	5810	0	s
5990	2	s	5808	0	s
5987	4	s	5805	4	s
5978	1	n	5792	1	s
5974	1	s	5787	1	s
5970	1	s	5782	1	s
5963	1	s	5696	6	s
5938	1	s	5692	4	s
5934	1	s	5687	2	n
5931	1	n	5682	4	s
5923	1	n	5642	3	n
5910	1	n	5635	2	n
5907	1	n	5631	1Sn?	n
5887	1	n	5619	1	s
5883	1	s	5614	1	s
5873	1	s	5611	1	s

Wave Length.	Intensity.	Character.	Wave Length.	Intensity.	Character.
5606	1	s	5348	1	s
5605	0	n	5340	1	s
5602	0	n	5336	1	s
5595	1	n	5334	2	s
5564	0	s	5330	1	s
5560	0	s	5328	1	s
5530	1	n	5327	1	s
5518	2	n	5324	1	s
5497	1	n	5322	2	s
5494	1	n	5317	2	s
5492	1	n	5313	1	n
5488	2	s	5307	1	s
5482	1	s	5304	1	s
5478	1	s	5302	1	s
5473	1	s	5298	3Cb?	n
5467	1	s	5294	8	s
5463	1	n	5289	3	s
5459	2	s	5062	8	s
5456	1	s	5055	2	s
5450	1	s	5052	2	n
5449	1	s	5050	1	s
5447	1	s	5047	1	s
5444	1	n	5045	2	n
5440	1	s	5044	1	s
5436	1	s	5040	2	s
5433	1	s	5034	3	s
5431	1	sD	5031	1	s
5420	1	s	5022	0	n
5418	1	s	5016	0	n
5413	1	s	5012	0	n
5410	1	s	5009	0	n
5407	1	s	5003	1	nD
5405	1	s	5000	0Ti-La?	n
5400	5	s	4996	0	n
5397	1Fe?	s	4993	1	n
5393	1	s	4989	1	n
5391	1	s	4988	1	n
5388	1	s	4986	1	n
5382	1	s	4980	2	s
5378	1	s	4976	2	s
5372	1	s	4972	1	s
5369	0	s	4870	1	n
5366	1	s	4965	1	n
5360	1	s	4951	3	s
5356	1	n	4949	1	s
5354	1	s	4940	1	s
5352	1	s	4938	1	s

Wave Length.	Intensity.	Character.	Wave Length.	Intensity.	Character.
4927 } 4865 }	2Fe.Ti.Cb? nb 2Fe.Ti.Cb? nb		4118	3	s
			4113	3	s
4850	2	n	4109	2	s
4847	1	n	4105	2	s
4837	2	s	4095	2	s
4834	2	s	4091	2	s
4829	3	n	4074	2	s
4826	3	n	4070	2	s
4823	2Mn?	s	3996	2	n
4821	1	s	3989	2	n
4819	1	s	3986	2	n
4815	0	s	3983	2	s
4812	2	s	3979	2 Cb?	n
4810	3	s	3975	2	s
4807	1	n	3971	2	s
4803	2	s	3969	2	s
4800	1	n	3961	4	s
4769	1	s	3956	2 Fe Ca	s
4764	1	s	3952	2	s
4754	1	s	3947	2	s
4752	1	s	3944	2	s
4686	2	s	3926	2	s
4656	2	n	3921	1	n
4637	2	s	3914	4	s
4582	1	s	3910	4	s
4577	1	s	3905	1	s
4458	1	s	3901	1	s
4432	1	s	3900	1	s
4430	1	s	3898	1	s
4427	1	s	3896	1	s
4424	1	s	3888	1	s
4421	1	s	3881	1	s
4397	1	s	3874	3	s
4387	1	s	3851	1	s
4376	1 Fe?	s	3787	3	s
4372	0	s	3785	3	s
4362	0	s	3781	2	n
4357	0	s	3778	4	s
4267	1	s	3774	2	s
4240	1	s	3770	2	s
4214	1	s	3768	1	s
4211	1	s	3764	2	s
4207	1	s	3691	3	s
4205	1	s	3686	3	s
4204	1	s	3682	4	s
4198	1	s	3678	7	s
4188	1	s	3672	3	s

Wave Length.	Intensity.	Character.	Wave Length.	Intensity.	Character
3670	5	s	3462	1	s
3669	3	s	3456	1	s
3667	1	s	3452	1	s
3665	3	s	3448	0 Cb?	s
3659	2	s	3446	0	s
3651	2	s	3440	5	n
3649	3	s	3430	0	s
3640	3 Fe?	s	3423	5	n
3639	2 Fe?	s	3414	0	3
3635	4	s	3412	0	s
3631	2 Fe?	s	3405	0	s
3620	4	s	3397	0	s
3612	2 Fe?	n	3395	0	n
3590	4	s	3393	0	n
3586	2	s	3390	0	n
3584	2	s	3387	0	n
3576	2	s	3385	0	n
3572	2	s	3383	0	n
3567	3	s	3380	0	n
3554	5	nD	3378	0	s
3547	5	n	3375	0	s
3545	1	s	3371	0	s
3542	5	nD	3368	0	s
3538	4	s	3366	0	s
3532	2	s	3361	0	s
3520	2	s	3347	0 Cb?	s
3507	3	n	3345	0	s
3503	2	s	3339	0	s
3499	2	s	3333	0	s
3496	2	s	3306	0 Fe?	s
3493	1	s	3300	0	s
3491	5 Cb?	n	3297	0	s
3489	1	s	3295	0	s
3487	1	s	3292	0	s
3485	5	n	3287	0	s
3482	1	s	3283	0	s
3480	1	s	3280	0	s
3475	2	n	3262	0	s
3471	2	s	3257	1	s
3470	1	n	3251	1	s
3466	1	n	3246	1	s

In the spectrum of columbium recently published by Hildebrand* there are several lines to be found, which correspond

*J. Am. Ch. S. 30, 1677.

both in wave length and in intensity, to lines found in the spectrum of tantalum. There is every reason to suppose that the Cb_2O_5 used by Hildebrand was as pure as could be prepared, with the present knowledge of columbium and its allied elements. And since we have the same assurance with regard to the Tb_2O_5 used in this work, there is either an unknown element associated with tantalum and columbium or a common impurity inseparable by the methods used in purification; for if the impurity in the specimen of Tb_2O_5 used by us was columbium, the lines should appear weaker in the tantalum spectrum, and vice versa.

Following, the coincident lines are given. To the right are the tantalum lines with intensity, to the left are Hildebrand's lines for columbium.

Wave Length.	Intensity.	Wave Length.	Intensity.
5366.0	1	5366	1
5340.1	1	5340	1
5321.9	2	5322	2
5317.1	2	5317	2
5302.4	1	5302	1
5054.9	2	5055	2
4992.6	1	4993	1
4764.0	1	4764	1
4357.0	1	4357	0
4203.6	1	4204	1
3764.2	2	3764	2
3667.1	1	3667	1
3496.2	2	3496	2
3387.1	1	3387	0
3361.0	1	3361	0
3262.0	1	3262	0

The following lines, which appear in the tantalum spectrum, do not appear in Exner and Hascheck's Spectrum of Columbium, but are attributed to this latter element by Hildebrand* and inserted in his table of wave lengths. To the right are the tantalum lines, to the left are Hildebrand's lines:

Wave Length.	Intensity.	Wave Length.	Intensity.
3888.6	1	3888	1
3287.1	1	3287	0
3257.2	1	3257	0

*Loc. cit.

The following strong lines are unidentified in Rowland's Solar Spectrum,* and are probably due to tantalum:

Wave Length.	Intensity.	Wave Length.	Intensity.
5682.427	2	5682	4
5012.335	1	5012	0
5031.199	3	5031	1
3910.469	2	3910	4
3910.670	2		
3682.310	2	3682	4
3554.593	2	3554	5
3538.643	1	3538	4
3538.399	1		

SPECTRUM OF A CLAY RESIDUE.

Below are given the wave lengths, which occur in the spectrum of precipitate A, and which have not been positively identified. The lines corresponding to Ti, Ta, Fe, Na, etc., have been removed from the table:

5890	2 Na?	s	4940	4	s
5885	2	s	4275	4 Cr?	s
5883	2	s	4110	3	n
5880	2	s	4100	3 Cb?	n
5875	3	s	4094	3	n
5866	2	n	3995	3	s
5860	3	n	3990	6	s
5853	3 Ba?	s	3982	6	s
5850	3	s	3973	7 Ca?	s
5844	8	s	3951	8	n
5834	8 Cb?	s	3942	9	n
5749	10	s	3931	6	n
5167	4 Mg?	s	3919	5 Cb?	s
4946	2 Cb?	s	3909	5 Cb?	s

The following lines are unidentified in Rowland's Solar Spectrum, and occur in the spectrum of precipitate A.

Wave Length.	Intensity.	Wave Length.	Intensity.
4094.573	2n	4094	3n
3995.352	2	3960	6
3990.248	0	3942	9
3942.510	2	3931	6
3942.380	0	2995	2
3931.030	0		

*See Rowland's Solar Spectrum.

SUMMARY.

1. The arc spectrum of tantalum has been measured between $\lambda 3200$ and $\lambda 6300$.

2. The method of using H_2SO_4 and HNO_3 for obtaining clays in solution, is satisfactory.

3. The spectrographic method for examining precipitates, for rare elements and traces, is pre-eminently superior to ordinary spectroscopy.

4. There is probably an unknown element associated with columbium and tantalum, or a common impurity, inseparable from either element, by ordinary means of purification.

5. There is a doubtful element or group of elements in the clay from Spruce Pine, Alabama.

6. Tantalum has been identified as one of the metals in the sun from lines which were marked unknown by Rowland.

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